

# Tip-induced domain growth on the non-polar cuts of lithium niobate single-crystals

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Currently, ferroelectric materials with designed domain structures are considered as a perspective material for new generation of photonic, data storage, and data processing devices. Application of external electric field is the most convenient way of the domain structure formation. Lots of papers are devoted to the investigation of domain kinetics on polar surface of crystals while the forward growth remains one of the most mysterious stages due to lack of experimental methods allowing to study it. Here, we performed tip-induced polarization reversal on X- and Y-non-polar cuts in single-crystal of congruent lithium niobate which allows us to study the forward growth with high spatial resolution. The revealed difference in the shape and length of domains induced on X- and Y-cuts is beyond previously developed theoretical approaches used for the theoretical consideration of the domains growth at non-polar ferroelectric surfaces. To explain experimental results, we used kinetic approach with anisotropy of screening efficiency along different crystallographic directions.

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Ferroelectrics are considered as perspective materials for wide range of acousto- and opto-electronic,<sup>1,2</sup> data storage, and computational devices.<sup>3,4</sup> In the last several decades, the main attention of investigators has been focused on study of domain kinetics under the action of applied electric field. Scanning probe microscopy (SPM) currently provides broad range of the tools for comprehensive investigations of different aspects of the ferroelectric materials. On the one hand, Piezoresponse Force Microscopy (PFM) allows visualization of the static domains structures with nanometer spatial resolution.<sup>5,6</sup> On the other hand, SPM tip-induced polarization switching allows producing of the isolated domains and complex domain structures<sup>3,7</sup> as well as study of polarization reversal process in the area under the tip by means of local hysteresis loops.<sup>8</sup>

Uniaxial single-crystalline LiNbO<sub>3</sub> (LN) is used as a model material for investigations because of existence of the simple domain structure with two possible polarization directions and applicability of several high resolution methods of domain visualization.<sup>5</sup> Recent studies of LN domain structures with nanometer spatial resolution demonstrate several unexpected phenomena including formation of dendrite domain structures after switching in homogeneous electric field<sup>9</sup> and chaotic behavior due to interaction of domains in the chain.<sup>10</sup>

However, most papers to the date explore the lateral domain growth on the polar surfaces (Z-cuts) and have a lack of information about forward domain growth along polar direction due to major experimental difficulties. The first study of the forward domain growth was carried out in barium titanate.<sup>11</sup> These behaviors were studied by *in situ* observations during application of electric field between metal electrodes deposited on the polar surfaces and demonstrated the growth of the needle-like domains. A number of non-destructive visualization

studies of the static domain structure in the bulk and reconstruction of the domain kinetics<sup>12,13</sup> by Raman confocal microscopy have been reported recently. However, the spatial resolution of this method is limited.<sup>14</sup> Scanning electron microscopy and optical microscopy after selective chemical etching were used also for investigation of the forward domain growth.<sup>15</sup>

At the same time, using of SPM offers an alternative way for studying the domain growth on the non-polar cuts with nanometer spatial resolution. In this case, SPM can be used both for polarization reversal by local application of the electric field via conductive tip and for visualization of the resulted domain patterns. Few experimental studies of the formation of in-plane shallow surface domains on nonpolar ferroelectric surfaces were published recently and devoted to formation of the domains in LN by electron beam irradiation,<sup>15</sup> SPM tip-induced switching in strontium-barium niobate<sup>16</sup> and LN.<sup>17</sup> The theoretical considerations of the in-plane domain growth were recently done by Landauer-Molotski<sup>18</sup> and Landau-Ginzburg-Devonshire approaches.<sup>17</sup>

However, previous papers are mostly focused on the features of the domain shapes and consider only one of the possible non-polar cuts (mainly Y). Used theoretical approaches do not consider difference of domains growth kinetics between X- and Y-non-polar cuts.

Here, we studied experimentally the tip-induced polarization switching on X- and Y-non-polar cuts of the congruent LN (CLN) and LN doped by magnesium oxide (MgO:LN) single-crystals. Investigations showed principal difference of the shapes and main geometrical parameters of domains formed on X- and Y-cuts. Obtained phenomenon was explained in terms of the kinetic approach.<sup>17</sup>

The thickness of the investigated plates was 20 and 200  $\mu\text{m}$  for CLN and 400  $\mu\text{m}$  for MgO:LN. The surface

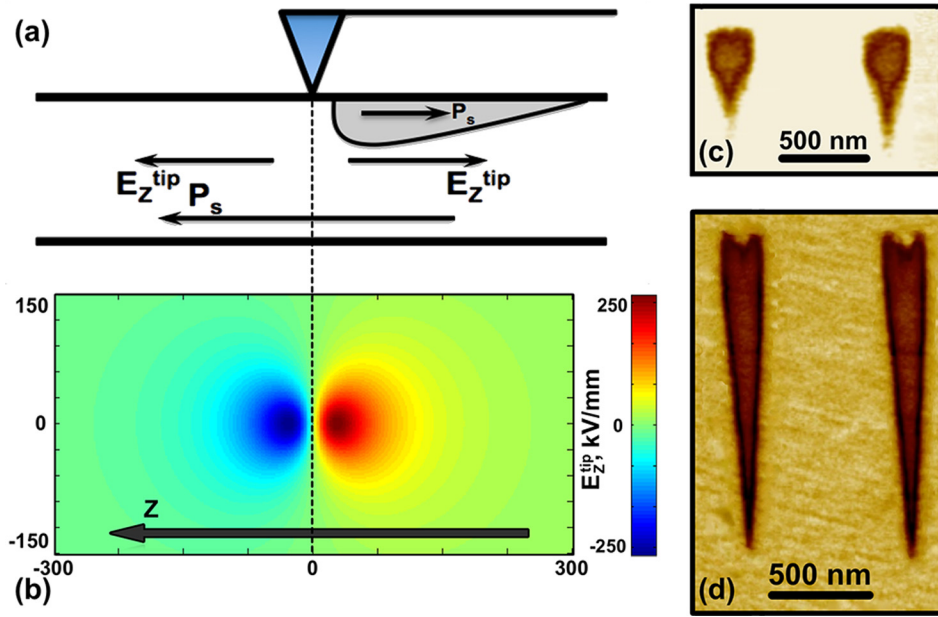


FIG. 1. (a) Scheme of tip-induced polarization reversal on non-polar cut of uniaxial ferroelectric. (b) Spatial distribution of polar Z-component of electric field produced by biased SPM tip.<sup>18</sup> (c) and (d) Domains formed as a result of tip-induced switching by single rectangular pulses with amplitude  $U_{sw} = 80$  V and duration  $t_{sw} = 1$  s on (c) X- and (d) Y-cuts of 20- $\mu$ m-thick CLN.

roughness for all samples was about 4 nm. Experiments were performed using the commercial scanning probe microscopes Dimension (Bruker, USA) and NTEGRA Aura (NT-MDT, Russia). Multi-75G-E (Budget Sensors, USA) and NSC-14 (Micromash, Estonia) SPM tips with a conductive platinum coating were used. Polarization reversal was performed by single rectangular pulses with amplitude  $U_{sw}$  ranged from 20 V to 200 V and with duration  $t_{sw}$  ranged from 100 ms to 60 s. Experiments were carried out at the room temperature in the atmosphere of dry nitrogen with zero relative humidity. Lateral piezoresponse force microscopy has been used for domain visualization at the sample surface.<sup>19</sup> Chemical etching in  $\text{HF}:\text{HNO}_3$  6:1 solution and atomic force microscopy (AFM) measurements of the topography of etched surface were used to reveal domain profile and depth in Y-cuts. For the revealing of domain shape in the bulk of X-cut sample, we used non-selective step-by-step chemical etching with PFM visualization between steps.

The tip-induced polarization reversal on non-polar cut of LN differs from the one on the polar cut due to the different distribution of the lateral component of electric field produced by the tip (Fig. 1(a)), which is directed radial with respect to the tip. This allows switching only in the area where electric field is directed against spontaneous polarization (Fig. 1(a)). However, our recent investigations also demonstrated formation of the domains in the opposite “prohibited” direction, which was attributed to backswitching phenomenon.<sup>17</sup> In the current manuscript, we applied the field pulses of one polarity which leads to mostly “normal” switching stage along applied electric field.

Formation of wedge-like domains prolated along polar Z-direction was obtained during polarization reversal in all studied samples (Figs. 1(c) and 1(d)). Domain sizes and shapes were found significantly different for X- and Y-cuts (Figs. 1 and 2).

The linear dependence of the domain length  $L$  and maximal width  $W$  on the switching pulse amplitude has been revealed (Figs. 3(a) and 3(b)). The domain width was found to be close to theoretically predicted values,<sup>18</sup> while the

length was found to be much longer and remarkably different for X- and Y-cuts. The domain aspect ratio was about three on the X-cut and ranged from 5.5 to 7.5 on the Y-cut. We should also note significantly high value of the error of width measurements. The obtained logarithmic dependence of the domain length on the duration of the pulse duration (Fig. 3(c)) is similar to results obtained in LN for switching on polar cut.<sup>20–23</sup> The backswitching during polarization reversal by long pulses (above 1 s) leads to irreproducible results for domain width (Fig. 3(d)).

At the same time, we did not find any significant dependence of the domain sizes and shapes on the sample thickness (in CLN). This fact is in a good agreement with spatial distribution of the tip-induced electric field, which is known to be localized in the small area in vicinity of the tip and is almost independent of the sample thickness. Domains in  $\text{MgO}:\text{LN}$  demonstrated considerably larger sizes due to lower value of the threshold field as compare with CLN.

The comparison of the experimental data with theoretical calculations presented in Ref. 18 showed unexpectedly large domain lengths. The maximum domain length on Y-cut in  $\text{MgO}:\text{LN}$  reached 30  $\mu\text{m}$ . However, the electric field produced by SPM tip is localized in a small area under the tip and negligibly small at such a long distance. The growth of domains far from the tip can be attributed to formation of the

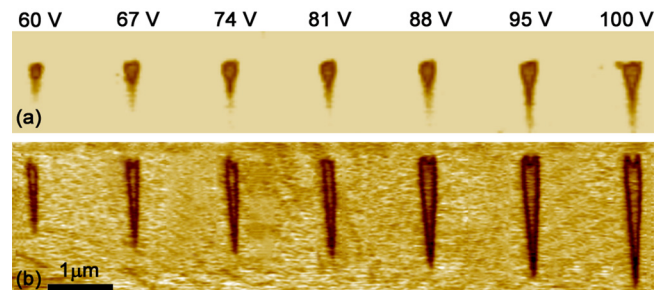


FIG. 2. Domains formed as a result of tip-induced switching by single pulse with various amplitudes and fixed duration  $t_{sw} = 1$  s in 20- $\mu$ m-thick CLN. (a) X-cut, (b) Y-cut.

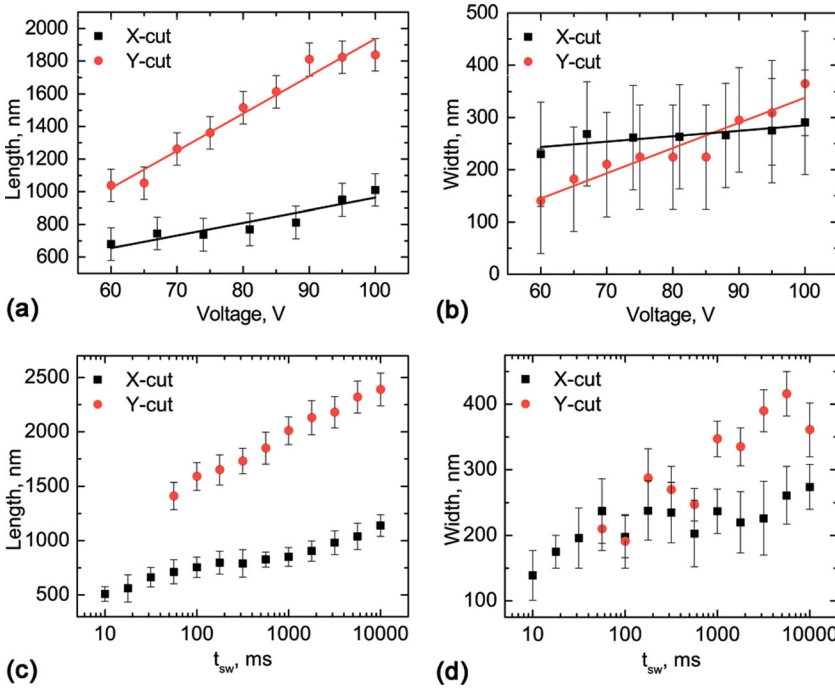


FIG. 3. Dependencies of (a) domain length and (b) domain width on the switching pulse amplitude, (c) domain length and (d) domain width on the switching pulse duration on 20- $\mu$ m-thick CLN X-cut and Y-cut.

metastable domain structures, due to screening of depolarization field during polarization reversal.<sup>24,25</sup> Thereby, we used kinetic approach to explain obtained experimental results.<sup>20,21</sup>

In the frame of the kinetic approach, the domain growth occurs by generation of elementary steps at the existed domain wall (2D nucleation) and their growth along the wall (1D nucleation).<sup>20,21</sup> Then, the nucleation probability is determined by the local value of the polar component of electric field ( $E_s$ ), which is represented by the superposition of the applied ( $E_z^{tip}$ ), depolarization ( $E_{dep}$ ), and screening ( $E_{scr}$ ) electric fields

$$E_s = E_z^{tip} + E_{dep} + E_{scr}, \quad (1)$$

$E_{scr}$  consists of two components: (a) fast external screening caused by redistribution of charges on the polar surfaces with characteristic time about 10 ÷ 100  $\mu$ s and (b) slow bulk screening by charge redistribution in the bulk with characteristic time ranged from 100 ms to 10<sup>3</sup> s.<sup>26,27</sup>

Application of the external field with component oriented against the direction of the spontaneous polarization leads to domain nucleation and subsequent growth which represents generation of the elementary steps near the tip at the polar surface and their motion along the wall in the polar direction (Fig. 4).

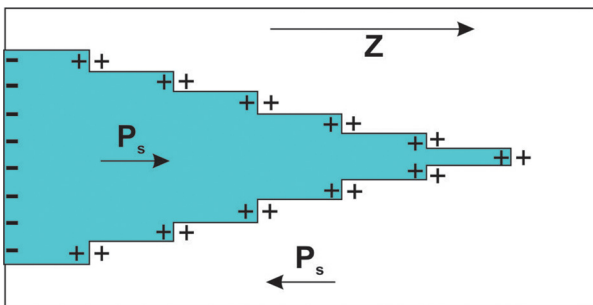


FIG. 4. The scheme of the domain growth on the non-polar cut of uniaxial ferroelectric.

According to kinetic approach, formation of the wedge-like domains with charged domain walls assumes that bound charges are localized at the elementary steps forming the domain wall (Fig. 4). The steps move under the action of the field produced by bound charges of the neighboring steps (Fig. 4). Thus, the domain elongation is caused by the interaction between the charged edges of the elementary steps. This mechanism allows to explain the domain growth in the areas far from the tip.

In terms of the proposed kinetic approach, obtained pronounced difference between domain shape and length on X- and Y-cuts can be attributed to different kinetics of the domain growth. Understanding of the domain kinetics requires investigations of the domain size and shape in the bulk. Detailed analysis of the PFM images demonstrates different qualitative distributions of the piezoresponse signal (Figs. 5(d) and 6(c)), which allows to assume the different domain configurations in the bulk.

To prove our assumption, we used chemical etching (selective and nonselective) to reveal domain depth and shape in the bulk. MgO:LN samples were used for the etching experiments due to lower coercive fields allowing to produce the larger domains. The analysis of the AFM images of resulted surface morphology showed that domains on the Y-cut represent the thin wedged plates with thickness about 10 nm (Figs. 5(e), 5(f), and 6(a)). At the same time, step-by-step nonselective etching of the domains on X-cut demonstrated that domains represent the hexagonal pyramids with tip situated in the bulk at the distance from the surface about hundreds of nanometers (Figs. 5(b), 5(c), and 6(b)). The etching during about 30 h demonstrated existence of the domain at the depth above 100 nm which is significantly deeper than domains on the Y-cuts. The formation of the subsurface domains on the X-cuts have been revealed after switching by both polarities of external electric field so it cannot be explained by the tilt of the crystallographic axes.



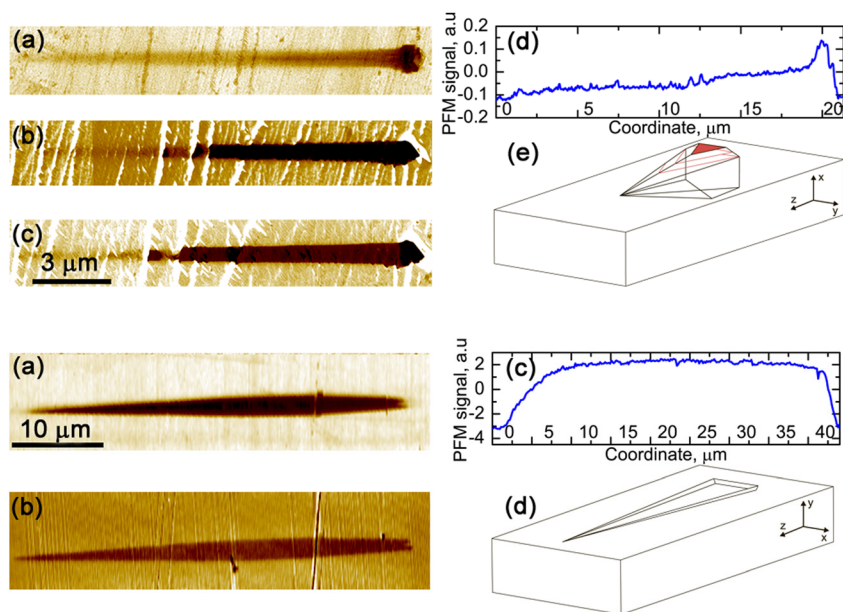


FIG. 5. PFM images of domain formed in X-cut: (a) as is; (b) after etching during 2.5 h, (c) after etching during 6 h, (d) distribution of PFM signal along the domain, (e) scheme of domain growth in the bulk with marked cross-sections revealed by the chemical etching. Applied voltage was 200 V, pulse duration was 60 s.

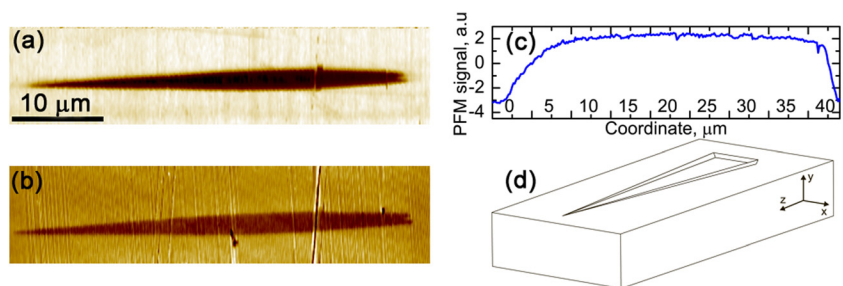


FIG. 6. (a) PFM image of domain formed in Y-cut, (b) corresponded etching profile, (c) distribution of PFM signal along the domain, (d) scheme of domain growth. Applied voltage was 200 V, pulse duration was 60 s.

The observed phenomena can be attributed to anisotropy of the bulk screening caused by anisotropy of bulk conductivity.<sup>20,28</sup> Such effect has not been revealed yet experimentally because of difficulties in measurement of bulk conductivity in LN at room temperature. However, it can be assumed by analogy with photogalvanic effect explored in LN along Y crystallographic axis.<sup>29</sup> As a result, domain steps generated in the depth have lower velocity of the propagation along the Z-direction due to lower value of the external electric field. It leads to retardation of the pyramid-shaped domain growth and results in a shorter domain length. Moreover, we cannot measure the total domain length in X-cuts by PFM because of the depth sensitivity is above 40 nm.<sup>6</sup>

An alternative explanation of the screening anisotropy can be attributed to band bending effect near the charged domain walls.<sup>30</sup> In this case, consideration of the nonlinear contribution to the screening process makes screening very sensitive to the local crystallographic asymmetry and thereby leads to screening anisotropy.

In conclusion, it was experimentally shown that the tip-induced polarization reversal on X- and Y-non-polar cuts in single-crystal of congruent lithium niobate demonstrates significant difference from the one on the polar cuts. The comparison of the experimental data with theoretical estimations<sup>18</sup> showed unexpectedly large length of obtained domains on Y-cut (reached 30  $\mu\text{m}$  for MgO:LN) and qualitatively different wedge-like shapes. All studied samples demonstrated the similar behavior. The domain growth in the area far from the tip with negligible value of the applied field was explained in terms of kinetic approach. It was proposed that the domain wall consists of elementary steps with localized bound charges which stimulate the growth of the neighboring steps. The obtained remarkable difference in the domain shape and length on the X- and Y-cuts has been attributed to distinction of the domain growth kinetics in the polar direction. The comparative analysis of the etched relief and PFM images proved that the domains on the Y-cut represent thin wedged plates, while the domains on the X-cut

possess the shape of hexagonal pyramids with tip situated in the bulk (Fig. 6). The lower value of the switching field in the bulk leads to shorter domains at X-cut.

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